

**CORRECTED  
VERSION\***

**PCT**

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>G03F 7/00, 7/16, G02B 1/06, B29D 11/00</b>		(11) International Publication Number: <b>WO 96/29629</b>	
<b>A3</b>		(43) International Publication Date: 26 September 1996 (26.09.96)	
(21) International Application Number: <b>PCT/US96/03073</b>		(72) Inventors: WHITESIDES, George, M.; 124 Grasmere Street, Newton, MA 02158 (US). XIA, Younan; 29 Greene Street #2, Somerville, MA 02143 (US). WILBUR, James, L.; 382 Massachusetts Avenue #601, Arlington, MA 02174 (US). JACKMAN, Rebecca, J.; 49 Harrison Street #1, Somerville, MA 02143 (US). KIM, Enoch; 321 Dartmouth Street, Boston, MA 02116 (US). PRENTISS, Mara, G.; Apartment 2, 1000 Memorial Drive, Cambridge, MA 02138 (US). MRKSICH, Milan; 325 Franklin Street #201, Cambridge, MA 02138 (US). KUMAR, Amit; 353 Silverlake Court, MilPitas, CA 95035 (US). GORMAN, Chris; 5104 Laurie Drive, Raleigh, NC 27606 (US). BIEBUYCK, Hans; Mythenstrasse 8, CH-8800 Thalwil (CH). BERGGREN, Karl, K.; Apartment #2, 34 Properzi Way, Somerville, MA 02143 (US).	
(22) International Filing Date: 1 March 1996 (01.03.96)			(74) Agent: OYER, Timothy, J.; Wolf, Greenfield & Sacks, P.C., 600 Atlantic Avenue, Boston, MA 02210 (US).
(30) Priority Data: 08/397,635 1 March 1995 (01.03.95) US 08/485,457 7 June 1995 (07.06.95) US			(81) Designated States: European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(71) Applicant: PRESIDENT AND FELLOWS OF HARVARD COLLEGE [US/US]; 124 Mount Auburn Street, Cambridge, MA 02138 (US).			Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
		(88) Date of publication of the international search report: 17 April 1997 (17.04.97)	

(54) Title: MICROCONTACT PRINTING ON SURFACES AND DERIVATIVE ARTICLES

(57) Abstract

Improved methods of forming a patterned self-assembled monolayer on a surface and derivative articles are provided. According to one method, an elastomeric stamp is deformed during and/or prior to using the stamp to print a self-assembled molecular monolayer on a surface. According to another method, during monolayer printing the surface is contacted with a liquid that is immiscible with the molecular monolayer-forming species to effect controlled reactive spreading of the monolayer on the surface. Methods of printing self-assembled molecular monolayers on nonplanar surfaces and derivative articles are provided, as are methods of etching surfaces patterned with self-assembled monolayers, including methods of etching silicon. Optical elements including flexible diffraction gratings, mirrors, and lenses are provided, as are methods for forming optical devices and other articles using lithographic molding. A method for controlling the shape of a liquid on the surface of an article is provided, involving applying the liquid to a self-assembled monolayer on the surface, and controlling the electrical potential of the surface.

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

REST AVAILABLE COPY

# INTERNATIONAL SEARCH REPORT

Internat Application No  
PCT/US 96/03073

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G03F7/00 G03F7/16 G02B1/06 B29D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03F G02B B29D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 142, no. 2, February 1995, pages 628-633, XP002015603 KIM E ET AL: "COMBINING PATTERNED SELF-ASSEMBLED MONOLAYERS OF ALKANETHIOLATES ON GOLD WITH ANISOTROPIC ETCHING OF SILICON TO GENERATE CONTROLLED SURFACE MORPHOLOGIES" see the whole document ---	1-11, 21-26, 62-64
X	US 4 528 260 A (KANE JAMES) 9 July 1985 see the whole document ---	34-40
X	US 3 497 377 A (ALLINGHAM WILLIAM D) 24 February 1970 see the whole document ---	56
A	---	49,50
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*&\* document member of the same patent family

Date of the actual completion of the international search

21 February 1997

Date of mailing of the international search report

12. 03. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Haenisch, U

REST AVAILABLE COPY

# INTERNATIONAL SEARCH REPORT

Internat Application No  
PCT/US 96/03073

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 018 829 A (OGAWA KAZUFUMI) 28 May 1991 see the whole document ---	65
P,X	WO 95 12480 A (MASSACHUSETTS INST TECHNOLOGY) 11 May 1995 see the whole document ---	57-59
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 504 (P-1127), 5 November 1990 & JP 02 210302 A (HAMAMATSU PHOTONICS KK), 21 August 1990, see abstract ---	56
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 376 (P-1092), 14 August 1990 & JP 02 140702 A (FUJITSU LTD), 30 May 1990, see abstract ---	56
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 420 (M-1023), 11 September 1990 & JP 02 165933 A (SEIKO EPSON CORP), 26 June 1990, see abstract -----	57-59

# INTERNATIONAL SEARCH REPORT

Int ernational application No.

PCT/US 96/03073

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. Claims : 1-43,60-65 methods for applying self-assembled monolayers patterns and their use in various etching, patterning and shaping process.
2. Claims : 44-59 optical elements having at least one reflecting surface characterized in that a liquid metal is used as reflecting material (optionally encapsulated in an elastomeric matrix)

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

BEST AVAILABLE COPY

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat. Application No  
PCT/US 96/03073

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4528260	09-07-85	NONE	
US-A-3497377	24-02-70	NONE	
US-A-5018829	28-05-91	JP-C- 1758021	20-05-93
		JP-B- 4044722	22-07-92
		JP-A- 61121016	09-06-86
		US-A- 4875759	24-10-89
WO-A-9512480	11-05-95	US-A- 5435887	25-07-95

BEST AVAILABLE COPY